Journal of Environmental Engineering and Landscape Management
ISSN 1648–6897 / eISSN 1822-4199
2021 Volume 29 Issue 2: 101–110
https://doi.org/10.3846/jeelm.2021.14190

Special issue on *Waste Valorisation for Sustainable Production, Process and Products*

RISK ASSESSMENT OF HEAVY METALS IN SOILS CONTAMINATED BY SMELTING WASTE FOR THE PERSPECTIVE OF CHEMICAL FRACTION AND SPATIAL DISTRIBUTION

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Received 28 February 2020; accepted 01 December 2020

Highlights

- The contents of heavy metal fractions (Pb and Cd) decrease with the soil depth.
- Three heavy metals (Cr, Cd, and Pb) were dominated by Fe-Mn oxides fraction.
- In this smelter, Cr mainly geogenic background sources, Cd and Pb derived from human activities.
- To those areas, provide some initial data on the heavy metal pollution remediation.

Abstract. The heavy metals contamination in soil has attracted increasing attention. In this study, the main objective was to determine three heavy metals (Cd, Pb, and Cr) of soils contaminated by smelting waste, and to evaluate pollution risk. The Pb (15.48 mg/kg) and Cd (311.39 mg/kg) mean concentrations exceeded the national standard, while Cr (48.60 mg/kg) concentration did not exceed. The Heavy metal fractions analysis showed that three heavy metals were dominated by Fe-Mn oxides fraction (Fe-Mn). The correlation and cluster analysis indicated that there was significant correlation between Cd and Pb ($0.55< r < 0.96$), while Cr was not correlation to Cd and Pb. The environmental pollution of heavy metals was assessed by the ratio of secondary phase and primary phase (*RSP*). The result showed that *RSP* values of Cd, Pb, and Cr range from 13.05–54.28, 16.11–4.97 and 1.61–52.33, which indicated soil was serious contaminated by them. These results showed that smelting waste discharge led to this smelter soil being seriously contaminated by multiple heavy metals which have a tendency to transport and accumulate into deep soil due to their high fractional transformation.

Keywords: heavy metals, smelting waste, spatial distribution, *RSP*.

Introduction

With urbanization and industrialization, soil pollution has become more serious, and heavy metals are major pollution element due to their toxicity and accumulation. Heavy metals not only threaten humans' health, but also affect plant metabolism (Cao et al., 2018). For example, people who exposure to Cd, Cr, and Pb environment long-term would more easily suffer human fatal diseases (Lu et al., 2018). Cd can affect plant active oxygen metabolism which induce physiological disorder of plant (Dong et al., 2010). The soil around smelter was polluted by smelting waste that produced during smelting process (including wastewater, soild waste and waste gas), which enrich heavy metals in soil greatly (Cai et al., 2015). Zhang

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et al. (2019) studied pollution characteristics and ecotoxicity in soil nearby silver smelting site, and found soil was heavily polluted by As, Cd, Pb, Zn, and Cu. Therefore, soil remediation around smelters has attracted increasing attention, where soil pollution can be avoided by removing heavy metals from smelting waste. At present, methods of removing heavy metals from smelting waste mainly include physical, chemical and biological methods (Steliga & Kluk, 2020; Zhu et al., 2015). Mo et al. (2018) summarized the latest developments in removing heavy metals from wastewater by agro-industrial waste as adsorbents, and thought it was a promising and effective technology. Ananya and Manan (2020) reviewed various treatment methods for decreasing ecotoxicological effects of wastewater, and thought bioremediation was the most sustainable and economically viable option. However, the soils that have been contaminated by smelting waste require comprehensive investigation then be given appropriate remediation methods.

Zhuzhou is the second largest city in Hunan province and is an industrial city beside the Xiangjiang River. There are more than one hundred factories in this city, including smelters, chemical factories, dyehouses, electroplating factories. The municipal sewage and industrial wastewater were discharged into the Xiang River, resulting in serious pollution, especially soil heavy metals pollution (Li et al., 2018). In the last ten years, soil pollution has been treated with varying ways in Zhuzhou (Wei et al., 2018). However, the problem is still serious because heavy metals are easy to transfer and diffuse in soil, water, and air (Nagajyoti et al., 2010). It is of great urgency to understand the pollution characteristics of heavy metals in the soil, and select an appropriate remediation technology. In previous experiments, we have detected heavy metals content in soil around Zhuzhou smelter beside Xiangjiang River (Wei et al., 2013). In this study, spatial distribution of three heavy metals (Cd, Cr, and Pb) in contaminated soils by smelting waste beside Xiangjiang River was investigated to further understand the characteristics of soil pollution. The aims of this study were (1) to identify fractions distribution characteristics of heavy metals, (2) to evaluate degree of soil pollution by the ratio of secondary phase and primary phase (*RSP*), and (3) to provide those areas with some initial data on heavy metal pollution remediation.

1. Materials and methods

1.1. Collection of sample

The soil sample was taken from a smelter by the Xiangjiang River in Zhuzhou (Figure 1). In this area, the soil here is yellow red soil, and vegetation is bushes, and annual average precipitation and temperature are about 1471 mm and 17.2 °C, respectively. In addition, the spread of smelting waste easy to the surrounding residential areas and Xiang River because of northwest wind in winter and south wind in summer in this area. This study selected four sites (A is located in the smelter, B and D are located by Xiang River, and C is located next to residential area) to understand extent and scope of soil pollution in this area. Each sampling site included five different profile soil samples (0–100 cm). The column soil was collected using cylindrical iron sampler at each depth interval (20 cm), removed stones and uniformly mixed, then taked 1–2 kg of soil as a complete soil sample, marked as A20, 40, 60, 80, 100, B20, 40, 60, 80, and 100, C20, 40, 60, 80, 100, D20, 40, 60, 80, and 100. Each complete soil sample was divided into two portions, one for air drying, grinding to pass through 100-mesh sieve, and measuring heavy metal content. The other was stored at 4 °C before analyzed soil biochemical properties.

1.2. Sampling analysis

The five fractions of Cd, Cr, and Pb were extracted by Tessier SER. The concentration of heavy metals was measured by an inductively coupled plasma mass spectroscopy (ICP-MS) (Tessier et al., 1979). Soil moisture was determined

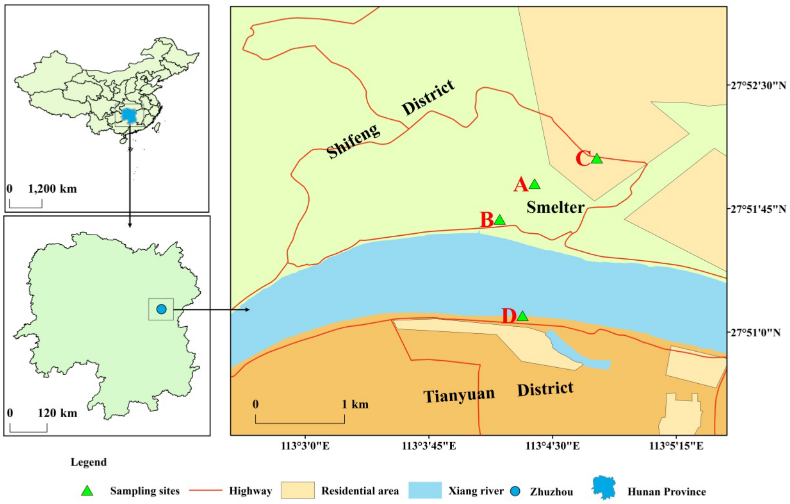


Figure 1. Four sampling sites. A: 113°4′23.46″E, 27°51′54.03″N, B: 113°4′10.74″E, 27°51′41.06″N, C: 113°4′46.09″E, 27°52′3.39″N, D: 113°4′19.06″E, 27°51′5.97″N

using oven-drying method. Soil pH in soil-water (1: 2.5) suspension was measured by a pH meter with a composite electrode (PHSJ-4F, China). Soil organic carbon was extracted using potassium dichromate volumetric method (Xu et al., 2019). Soil available nitrogen determination was performed by the method of Dorich and Nelson (Dorich & Nelson, 1984). The urease was extracted by sodium phenolate colorimetry, and the urease activity was detected by amount of NH_3-N in soil after experimental treatment 24 h. The catalase enzyme was obtained by measuring volume of required for $KMnO_4$ titration after adding hydrogen peroxide to the soil for 20 min. The dehydrogenase activity was determined using ultraviolet spectrometry method (Akhtar et al., 2018). Each experiment was replicated three times.

1.3. Ratio of secondary phase and primary phase (RSP)

Xia et al. (2018) proposed that primary minerals in sediments were regarded as primary phase, weathering products of primary minerals and exotic organisms as secondary phase. Ratio of secondary phase and primary phase was used to evaluate potential ecological risk of the soils and formula was as follows:

$$RSP = M_{sec}/M_{prim}. \tag{1}$$

The M_{sec} and M_{prim} were the secondary phase and primary phase values of soils. The *RSP* values of the classification criteria for heavy metals are listed in Table 1.

Table 1. Classification criteria of the Ratio of secondary phase and primary phase (*RSP*) (Xia et al., 2018)

Grade Type	1	2	3	4
RSP value	≤1	1~2	2~3	>3
Pollution level	clean	low	moderate	high

2. Results

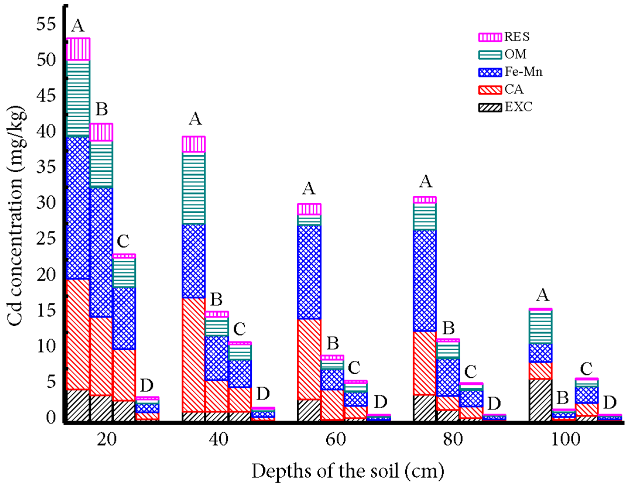
2.1. Soil properties and enzyme activity

Soil properties and enzymes are indicators of soil biological changes, and enzymes are sensitive indicators of changes in soil properties (Kravkaz et al., 2018). The vertical distributions of soil properties and enzyme activities at four sampling sites are shown in Table 2. Properties of soil pH, water contents, organic carbon, and available nitrogen were studied, and there were no significant variations for these depending on soil depth at four sampling sites. Soil pH shows acidity (pH mean values ranging from 4.71–6.40). During the enzyme activity, three enzyme activities are not significant variations in vertical section

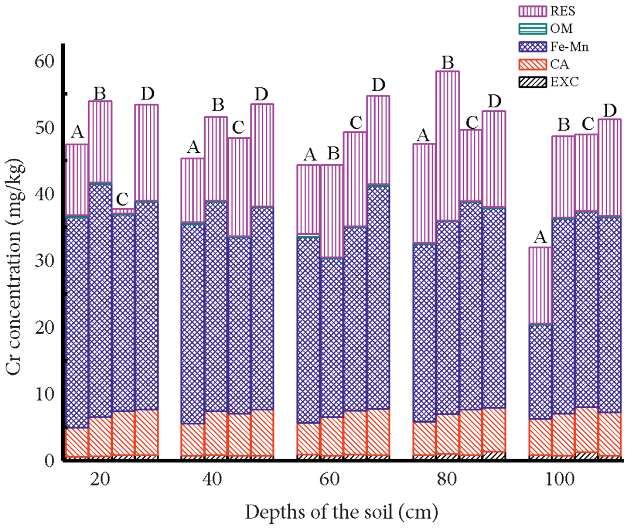
Table 2. The biochemical properties of soils at four sampling sites

Districts	pH	Water content (%)	Organic carbon (g/kg)	Available nitrogen (mg/kg)	Urease (mg/g.d)	Dehydrogenase (mg/g)	Catalase (mL/g.20min)
A20	5.61±0.38	0.20±0.01	67.43±4.72	84.56±5.07	4.22±0.01	19.23±1.65	1.40±0.03
A40	5.31±0.27	0.20±0.01	67.03±4.69	82.88±4.97	4.18±0.01	17.02±1.20	2.40±0.19
A60	5.34±0.37	0.16±0.00	68.47±4.79	66.98±4.01	4.33±0.01	12.60±0.89	2.30±0.18
A80	5.20±0.26	0.20±0.01	70.38±4.93	75.35±4.52	4.25±0.00	15.97±1.13	2.48±0.20
A100	5.59±0.28	0.23±0.01	69.67±4.88	71.16±4.26	4.31±0.00	13.12±2.20	1.00±0.01
B20	5.06±0.25	0.15±0.00	67.67±3.23	77.86±6.23	4.37±0.00	36.60±1.56	2.40±0.08
B40	5.98±0.30	0.19±0.00	68.79±9.34	78.70±6.30	4.44±0.00	41.65±7.89	2.15±0.17
B60	6.40±0.32	0.27±0.01	69.19±9.99	64.46±5.16	4.31±0.03	29.86±3.23	2.25±0.12
B80	6.04±0.30	0.22±0.01	66.71±5.67	81.25±7.30	4.12±0.01	23.23±4.34	0.45±0.12
B100	6.38±0.32	0.16±0.01	69.75±8.67	66.98±5.39	4.27±0.01	24.60±1.74	0.55±0.03
C20	5.28±0.26	0.14±0.00	58.97±9.56	70.32±1.41	4.30±0.00	27.44±1.24	0.15±0.00
C40	4.85±0.24	0.16±0.00	59.46±3.21	74.51±1.49	4.32±0.01	35.96±2.55	0.50±0.00
C60	4.73±0.23	0.14±0.00	69.43±2.34	68.65±1.37	4.13±0.01	23.33±1.66	0.70±0.00
C80	5.15±0.11	0.23±0.01	66.63±2.90	66.14±1.32	4.22±0.01	18.91±1.34	1.20±0.01
C100	4.71±0.00	0.16±0.00	82.67±7.89	77.02±3.54	4.27±0.00	23.12±1.64	2.45±1.20
D20	4.76±0.24	0.25±0.01	35.51±0.71	62.79±1.23	4.21±0.01	25.97±1.33	0.35±0.00
D40	4.38±0.23	0.25±0.01	40.30±0.80	74.51±1.49	4.26±0.02	25.65±1.82	0.45±0.01
D60	4.85±0.01	0.24±0.01	38.78±0.77	77.86±1.56	4.25±0.04	23.76±1.69	0.30±0.00
D80	4.23±0.36	0.21±0.01	46.28±0.92	77.86±1.45	4.38±0.06	22.28±1.58	0.40±0.00
D100	4.97±0.25	0.20±0.01	38.78±0.77	79.53±1.59	4.25±0.01	19.86±0.01	0.60±0.00

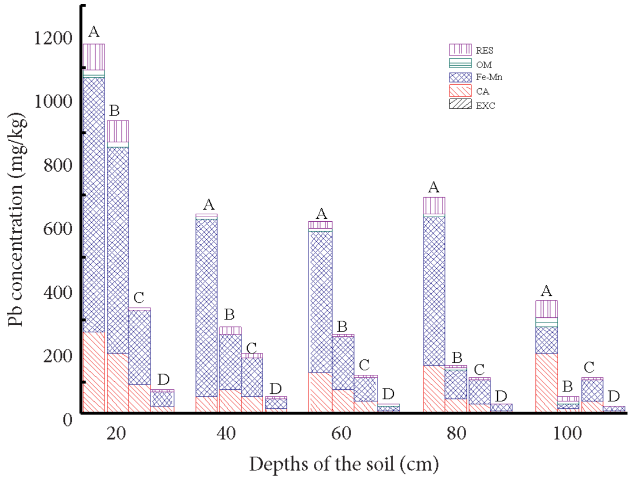
Note: A, B, C, and D represent four sampling sites. 20, 40, 60, 80, and 100 represent 20–100 cm of soil depth, respectively.



a) Distribution of heavy metal Cd



b) Distribution of heavy metal Cr



c) Distribution of heavy metal Pb

Figure 2. Distributions of three heavy metals at different depths in soil. EXC: exchangeable fraction, CA: carbonate fraction, Fe-Mn: Fe-Mn oxide fraction, OM: organic matter fraction, RES: residual fraction

at four sampling sites. But dehydrogenase and catalase enzyme are differences among four sampling sites, and mean values ranging from 15.58–31.18 mg/g and 0.42–1.91 mL/g.20 min.

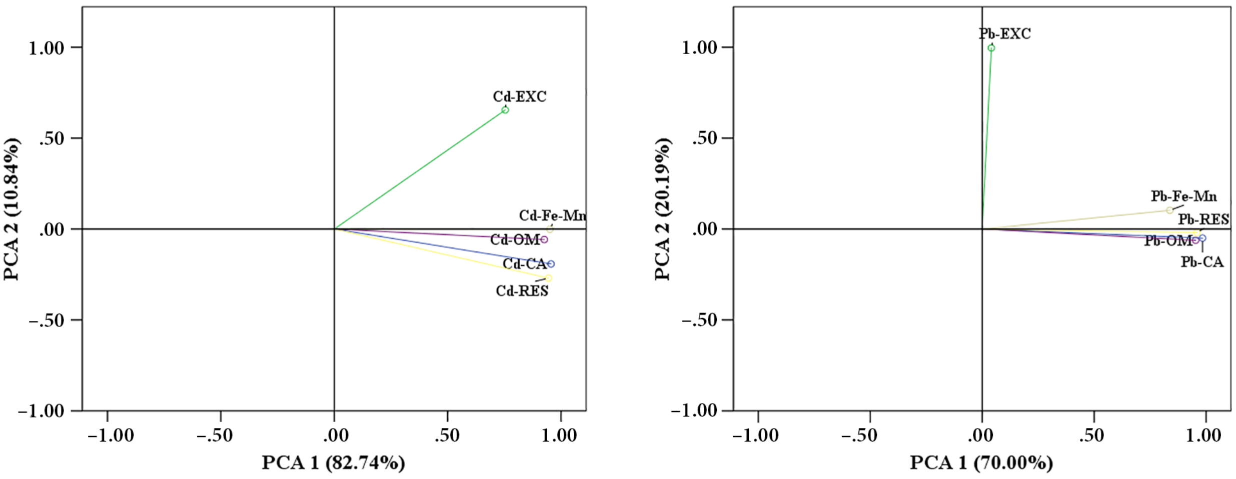
2.2. Distribution of heavy metals fraction

The heavy metal Cd, Cr, and Pb were extracted by using the Tessier SER in this study. Heavy metal fractions include exchangeable fraction (EXC), carbonate fraction (CA), Fe-Mn oxide fraction (Fe-Mn), organic matter fraction (OM), and residual fraction (RES). In general, CA and EXC fractions are easy to be utilized by living organisms, Fe-Mn fraction is unstable under low potential conditions, and RES and OM fractions of heavy metal could hardly be utilized and have minimal environmental impact (Huang et al., 2018; Rong et al., 2020).Vertical distributions of heavy metal fraction in four sampling sites of smelter are shown in Figure 2. In general, Cd and Pb contents decrease with depth of soil, and they follow order of A>B>C>D in the vertical section at the four sampling sites except 100 cm (A>C>B>D), while amount of Cr is no significant variation (minimum at 100 cm in A site is 31.93 mg/kg). The major fraction of Cd is Fe-Mn and CA at different depths of four sampling sites, excepting 100 cm in A site (the major fraction is EXC and accounted for 38.28% of total cadmium), while the major fraction of Cr is Fe-Mn and RES. For Pb, the major fraction is Fe-Mn at different depths of four sampling sites.

Figure 3 is the principal component analysis (PCA) of five fractions of Cd and Pb. The values of KMO in Figure 3 (a–b) are 0.679 and 0.672, respectively, and their Bartlett's Test p values are less than 0.05, and their Kolmogorov-Smirnov test p values are less than 0.05. These tests show principal component analysis is suitable for the study. The Figure 3 (a–b) shows that cumulative variance of contributions reach 93.58% and 90.19% for principal component of Cd, and Pb, respectively. The EXC fraction of Cd is clustered to one component accounting for 82.74% of variance, and the rest to second component accounting for 10.84% of variance. This is also same situation with Pb, and two component accountiong for 70.00% and 20.19% of variance, respectively. The analysis reveals that fractions of Cd and Pb are highly correlated, except for EXC fraction. For heavy metal Cr, the value of KMO is 0.333, and it's not suitable for principal component analysis. This also shows that five fractions of Cr have low correlation.

2.3. Correlation analysis

In order to explore the interaction between heavy metals in soil, this study analyzed correlation of five fractions of three heavy metals. The results are given in Table 3. There is a positive correlation between five fractions of Cd ($0.54 < r < 0.92$), and they are positively correlated with CA, Fe-Mn, RES, and OM fractions of Pb ($0.55 < r < 0.96$). A significant positive correlation is observed between Cd fraction and OM fraction of Cr ($0.46 < r < 0.78$) and a negative correlation ($-0.70 < r < -0.82$) with CA fraction of Cr.



a) Principal component analysis of Cd fraction b) Principal component analysis of Pb fraction

Figure 3. Principal component analysis of heavy metal Pb and Cd fractions. EXC: exchangeable fraction, CA: carbonate fraction, Fe-Mn: Fe-Mn oxide fraction, OM: organic matter fraction, RES: residual fraction

Among five fractions of Cr, only CA and OM fractions are correlated significantly. CA fraction is negatively (–0.64 < r < –0.79) correlate with CA, Fe-Mn, RES, and OM fractions of Pb. However, OM fraction is positively correlate with CA, Fe-Mn, and OM fractions of Pb (0.45 < r < 0.74) and low correlation with RES fraction of Pb. This result also explains why KOM value is low in Cr.

With regard to Pb, except for EXC fraction, other fractions are significantly correlated (0.65 < r < 0.95). In addition, the correlation between heavy metals and soil depths are presented in Table 3. These results indicate that Cd and Pb were significantly negative correlations with soil depths except RES fraction of Pb. On the contrary, Cr and soil depths are less relevant.

Heat map is a well-organized method of imaging multipart data sets prepared as matrices, and determining relationship between variables and clusters of variables by cluster analysis (Kükrer et al., 2015). The heat map for trace elements and soil characteristics are shown in Figure 4. Figure 4 display three clusters: (1)

Table 3. Correlation matrix between five fractions of different heavy metal

Fraction	Cd-EXC	Cd-CA	Cd-Fe-Mn	Cd-OM	Cd-RES	Cr-EXC	Cr-CA	Cr-Fe-Mn	Cr-OM	Cr-RES	Pb-EXC	Pb-CA	Pb-Fe-Mn	Pb-OM	Pb-RES	Depths
Cd-EXC	1	0.59**	0.70**	0.65**	0.54*	–0.24	–0.70**	–0.41	0.46*	–0.29	–0.13	0.92**	0.63**	0.94**	0.83**	–0.53*
Cd-CA		1	0.91**	0.87**	0.92**	–0.37	–0.82**	0.13	0.78**	–0.39	0.06	0.70**	0.96**	0.55*	0.56**	–0.58**
Cd-Fe-Mn			1	0.78**	0.90**	–0.37	–0.75**	0.20	0.71**	–0.27	0.02	0.83**	0.96**	0.68**	0.74**	–0.58**
Cd-OM				1	0.87**	–0.40	–0.73**	0.01	0.56**	–0.33	0.13	0.72**	0.86**	0.67**	0.65**	–0.54*
Cd-RES					1	–0.45*	–0.73**	0.27	0.75**	–0.23	0.20	0.72**	0.96**	0.61**	0.68**	–0.50*
Cr-EXC						1	0.25	–0.09	–0.31	0.17	–0.27	–0.383	–0.42	–0.33	–0.41	0.26
Cr-CA							1	0.28	–0.64**	0.08	.032	–0.75**	–0.79**	–0.67**	–0.64**	0.50
Cr-Fe-Mn								1	0.25	–0.02	0.29	–0.24	0.20	–0.35	–0.13	0.18
Cr-OM									1	–0.34	0.16	0.51*	0.74**	0.45*	0.44	–0.32
Cr-RES										1	0.10	–0.26	–0.29	–0.20	–0.08	0.31
Pb-EXC											1	–0.01	0.09	–0.01	0.03	0.42
Pb-CA												1	0.79**	0.95**	0.92**	–0.56**
Pb-Fe-Mn													1	0.65**	0.71**	–0.54*
Pb-OM														1	0.93**	–0.44*
Pb-RES															1	–0.41

Note: * represent significantly different at $P < 0.05$, ** represent significantly different at $P < 0.01$, EXC: exchangeable fraction, CA: carbonate fraction, Fe-Mn: Fe-Mn oxides fraction, OM: organic matter fraction, RES: residual fraction.

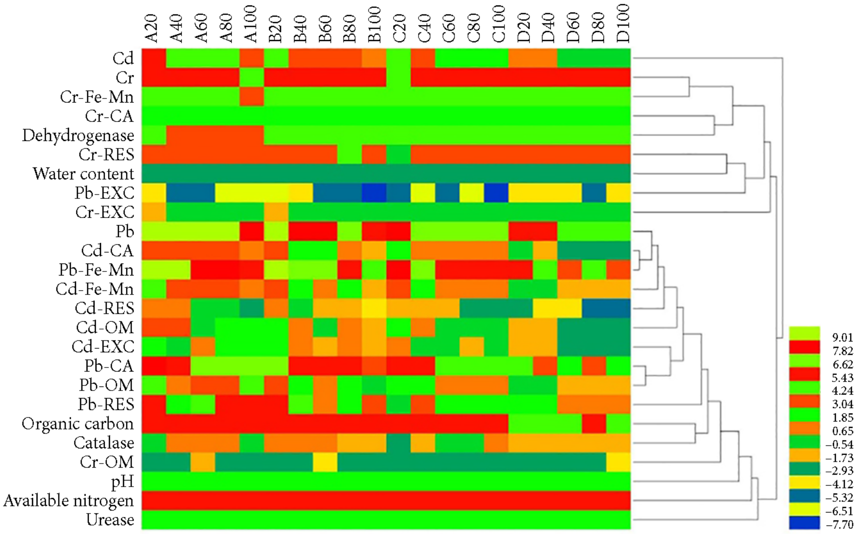


Figure 4. Hierarchical clustering analysis of trace elements and soil characteristics at four sampling sites. EXC: exchangeable fraction, CA: carbonate fraction, Fe-Mn: Fe-Mn oxides fraction, OM: organic matter fraction, RES: residual fraction. A, B, C, and D are sampling sites. 20, 40, 60, 80, and 100 are soil depths

Total Cd. (2) Total Cr, Pb-EXC, dehydrogenase, water content, and Cr fraction (except Cr-OM), and these elements are mainly geogenic background sources. (3) Total Pb, Cr-OM, enzyme activity (except dehydrogenase), organic carbon, available nitrogen, pH, and Cd and Pb fractions (except Pb-EXC), and these elements may be derived from anthropogenic activity. Cd and Pb fractions are clustered together, which indicate a common source of migration (Xia et al., 2018). The results are consistent with correlation matrix and principal component analysis.

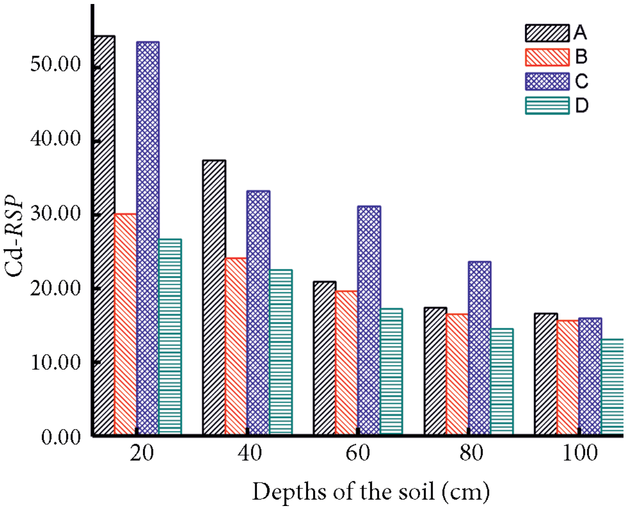
2.4. Ratio of secondary phase and primary phase (RSP) analysis

The chemical speciation information is of fundamental importance for practical environmental risk assessment of soil associated with heavy metals (Zhang et al., 2017). In this study, *RSP* evaluated intensity of human activities on soil. The *RSP* indices of three heavy metals are given in Figure 5. For Cd (Figure 5a), the *RSP* values are between 13.05 and 54.28, which the *RSP* values are over 3, so the soil is heavily contaminated with Cd at the four sampling sites. The average *RSP* values for Cd of four sampling sites follow the order of C>A>B>D. For Cr (Figure 5b), the *RSP* values range from 1–4 except for 52.33 in the site C 20 cm, of which 45%, 45% and 10% of soil samples are serious, moderate and low pollution levels. For Pb (Figure 5c), its pollution trend is similar to Cd at four sampling sites, but its *RSP* value is less than Cd. The values of *RSP* are higher than 4, and maximum was 16.11 at 20 cm in the site C. The Figure 5 shows that *RSP* values of Cd and Pb decreases with the depth of soil at the sites A, B, C, and D. The *RSP* value of Cr has no obvious change in depth of soil, while it is too high in the site C 20 cm ~~of~~. These results are consistent with total heavy metal analysis except for *RSP* assess soil was pollution with Cr. It confirms that soil may suffer anthropogenic activity, resulting in higher calculated *RSP* value.

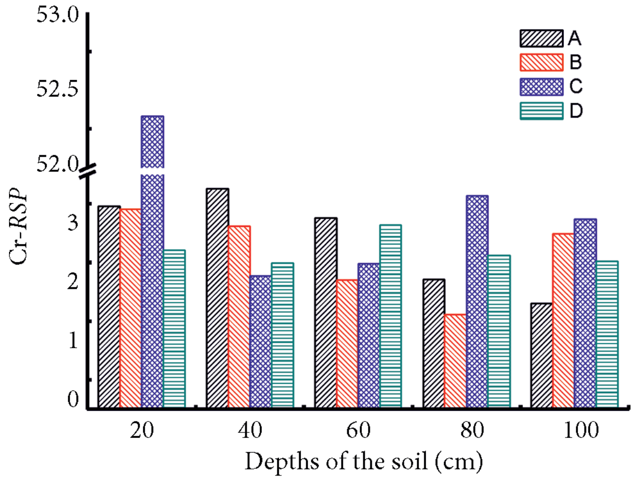
3. Discussion

The soil pH is affected by heavy metal, smelting waste, and geographic locations (Lenart & Wolny-Koladka, 2013). In this study, the soils of four sampling sites were acidic. The primary cause was that the soil of South China was affected by acidic rainfalls and this smelter often discharges acidic wastewater, waste gas (Wang & Wang, 1995). Interestingly, the available nitrogen and organic carbon contents were very high, but the soil enzyme activity was lower. The possible reason was that soil microorganisms might exhibit metabolic dysfunction under smelting waste stress (Gupta & Diwan, 2017). The biomass was less effective in mineralised organic matter under metal stress, resulting in high organic carbon content (Valsecchi et al., 1995). Additionally, soil properties and enzyme activities were no significant change in the vertical section at different districts, similar conclusion were drawn by most of the studies (Beattie et al., 2017). In general, soil biochemical properties may have been altered under this smelter discharge of smelting waste will require further research on soil (Zhang et al., 2011; Shen et al., 2018).

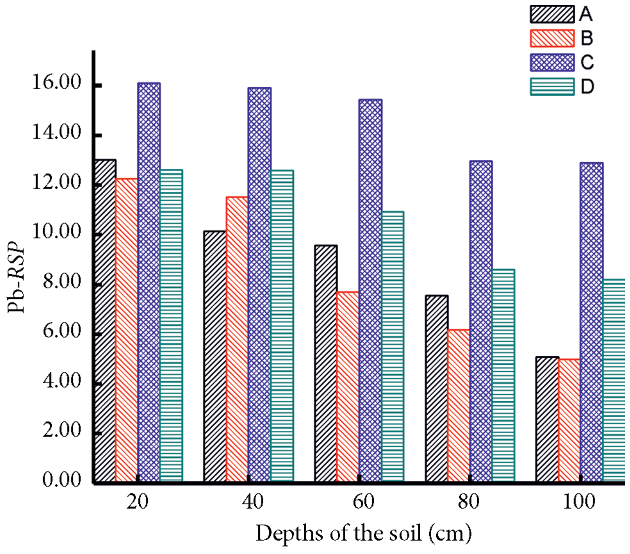
The topsoil of the smelter is susceptible to anthropogenic activity, resulting in heavy metals contents increase (Sun & Mou, 2016). In addition, heavy metals contents in soil around a smelter vary with the different sites (Shen et al., 2017). Therefore, soil profile was studied from 0 to 100 cm at the four sampling sites of smelter in this



a) The value *RSP* of Cd



b) The value *RSP* of Cr



c) The value *RSP* of Pb

Figure 5. *RSP* of three heavy metals at different depths in the soils

study. The results indicated that total Cd content of all sampling soils exceeded secondary standard maximum allowable value of environmental quality standard for soil (GB15618-1995) (Cui et al., 2018). On the contrary, total Cr content did not exceed by the concentration limit. Total Pb content did not exceed the concentration limit in site B 60–100 cm and sites A 40–100 cm and C, possibly due to it had allochthonous origins, such as through surface runoff and industrial drainage (Kükrer, 2018). The amounts of total Cd and Pb were decreased with depth of the soil. Shen et al. (2017) explored soil near a Pb/Zn smelter, the results show that soil Cd and Zn contents decreased vertically. Sun et al. (2013) surveyed spatial distribution of heavy metals in agricultural soil, Cu and Pb were negative correlation with soil depths. Strangely, the total Cr amount had no significant change in the soil depth. In brief, the soil suffered Cd and Pb multiple polloution, and heavy metal Cr existed in an extremely stable form.

In this study, at different depths, three heavy metals were dominated by Fe-Mn fraction, except for a few cases. Possible reason was that the soil was subject to severe emission of metal ion-containing wastewater and soild waste (Ye et al., 2019). A large number of metal ions were present in soil, which will promote formation of Fe-Mn fraction (Zhong et al., 2014). At different sampling sites, all fractions of Cd and Pb followed the order of A>B>C>D, but site C fraction exceed site B in 100 cm, reason was that site B soil was tighter than site C, resulting in heavy metal migration slowed with soil depth (Nabulo et al., 2010). The Cr fraction did not obviously change in four sites, and RSP value was extremely high in site C 20 cm. This means that C site topsoils suffered serious erosion. In general, the site A was most affected due to it was most adjacent to smelting waste site source. On the contrary, site D was farthest and was lowest affected. These results showed that the soil was severely eroded and degree of influence was related to distance of pollution source.

The heavy metals distribution in soil is affected by various factors (such as total heavy metals and chemical speciation, anthropogenic activity and geogenic background, etc.) (Huang et al., 2018). Pearson's correlation analysis can reflect the degree of influence between them. There was high correlation between Cd and Pb fractions. But EXC fraction of Pb was not correlated with five fractions of Cd, and its concentration was relatively low. The principal component analysis (PCA) also showed the same result. These results could be explained if EXC fraction has been converted to other chemical fractions or most have been absorbed by local vegetation (Nabulo et al., 2010). The Cr was no correlation with other except OM and CA fractions. This indicated that Cd and Pb in the smelter soils were unstable, their chemical speciation was converted. The Cr was relatively stable, but it was potentially toxic because of the correlation between OM and CA fractions ($P < 0.01$). It maybe due to the smelter was corroded by Fe and Mn ions, that they could oxidize and reduce Cr ion to achieve fractional transformation (Jobby et al., 2018). There was no doubt that transformation of heavy metal chemical fractions during heavy metal pollution in soil is inevitable (Ancona et al., 2020). Combining with source analysis and *RSP* assessment results shows: this smelter's anthropogenic activity was same source of Cd and Pb, while heavy metal Cr was derived from anthropogenic activity and geogenic background.

Conclusions

In the past few years, heavy metal pollution prevention and control have made rapid progress in Zhuzhou, but this problem was still serious. Conducting field investigation and analyzing the heavy metals properties in typical contaminated areas to fully understand the process, extent, and source of heavy metal pollution will improve remediation effect. This study explored spatial distributions of three heavy metals Cd, Cr and Pb in soil around Zhuzhou smelter beside Xiangjiang River, and conducted a series of analyses. From the above results, the following conclusions can be drawn: Cd and Pb contents of this smelter exceeded secondary standard maximum allowable value of Environmental quality standard for soil (GB15618-1995), while Cr content did not exceed. Pb, Cd and Cr of this smelter were dominated by Fe-Mn fraction. The *RSP* assessment concluded that serious polluted by heavy metal Pb and Cr, while Cr typically at a moderate level, except for a few cases. The correlation and cluster analysis shown that Cd, Pb, and partly Cr derived from anthropogenic activity, and geogenic background was Cr main source. It can be speculated that this smelter suffered serious anthropogenic activity (corrosion of metal ions from smelting waste), leading to heavy metal fractions transforming to Fe-Mn fraction. Therefore, this smelter should be more focused on removing metal ions from smelting waste to improve remediation efficiency.

Author contributions

Xiaoxi Zeng, Qiming Chen, and Wen Li: Conceptualization, Methodology, Software. Hong Xu, Xiaoxi Zeng, and Qiming Chen: Data curation, Writing-Original draft preparation. Jiali Ren, Feijun Luo, and Ling Wu: Visualization, Investigation. Jianxing Tang: Supervision. Dongmin Liu and Hong Xu: Software, Validation. Xiaoxi Zeng, Qiming Chen, Qing Tan, Sheng Yang, Jianhui Wang, and Yuanke Zhang: Writing-Reviewing and Editing.

Acknowledgements

This research was funded by National Science and Technology Program during the Twelfth Five-year Plan Period, China (2015BAD05B02 and 2018YFE0110200), High Technology Industry S & T Innovation Leading Project of Hunan Province (2020NK2001), The Natural Science Foundation of Hunan Province of China (2018JJ2090 and 2020JJ4278), The National Natural Science Foundation of China (51774128 and 51774129), The Key Program of the Hunan Provincial Department of Science and Technology (2020WK2020), Program for Science & Technology Innovation Platform/Talents of Hunan Province (2019TP1029) and Social Development and Livelihood Program of Zhuzhou City of China (2018 and 2019).

Conflict of interests

The authors declare that there is no conflict of interest regarding the publication of this paper.

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